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⑦① Applicant: **ATLANTIC RICHFIELD COMPANY, 515 South**  
**Flowers Street, Los Angeles California 90071 (US)**

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⑦② Inventor: **Yoo, Jin Sun, 2315 Mast Court, Flossmoor**  
**Illinois 60422 (US)**  
Inventor: **Jaecker, John Alvin, 2352 Clyde Terrace,**  
**Homewood Illinois 60430 (US)**

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⑦④ Representative: **Cropp, John Anthony David et al,**  
**MATHYS & SQUIRE 10 Fleet Street, London, EC4Y 1AY**  
**(GB)**

⑤④ **A process for combusting sulfur-containing material, a hydrocarbon conversion process including such a combustion process in a catalyst regeneration step and a composition suitable for use as a catalyst in the hydrocarbon conversion process.**

⑤⑦ In a process for converting hydrocarbons using a catalyst which is periodically regenerated to remove carbonaceous deposits, the amount of sulfur oxides exiting the catalyst regeneration zone is reduced by using a conversion catalyst comprising a mixture containing, as a major component, solid particles capable of promoting hydrocarbon conversion at hydrocarbon conversion conditions, and, as a minor component, discrete entities comprising at least one spinel, preferably an alkaline earth metal-containing spinel.

The mixture of solid particles and discrete entities and a process for reducing the concentration of sulfur oxide emitted from a process of combusting sulfur-containing material by effecting the combustion in the presence of metal-containing spinel are also disclosed.

**EP 0 045 170 A1**

BACKGROUND OF THE INVENTION

The invention is concerned with the combusting of solid, sulfur-containing material in a manner to effect a reduction in the emission of sulfur oxides to the atmosphere. In one specific embodiment, the invention involves the catalytic cracking of sulfur-containing hydrocarbon feedstocks in a manner to effect a reduction in the amount of sulfur oxides emitted from the regeneration zone of a hydrocarbon catalytic cracking unit.

Typically, catalytic cracking of hydrocarbons takes place in a reaction zone at hydrocarbon cracking conditions to produce at least one hydrocarbon product and to cause carbonaceous material (coke) to be deposited on the catalyst. Additionally, some sulfur, originally present in the feed hydrocarbons, may also be deposited, e.g., as a component of the coke, on the catalyst. It has been reported that approximately 50% of the feed sulfur is converted to  $H_2S$  in the FCC reactor, 40% remains in the liquid products and about 4 to 10% is deposited on the catalyst. These amounts vary with the type of feed, rate of hydrocarbon recycle, steam stripping rate, the type of catalyst, reactor temperature, etc.

Sulfur-containing coke deposits tend to deactivate cracking catalyst. Cracking catalyst is advantageously continuously regenerated, by combustion with oxygen-containing gas in a regeneration zone, to low coke levels, typically below about 0.4% by weight, to perform satisfactorily when it is recycled to the reactor.

In the regeneration zone, at least a portion of sulfur, along with carbon and hydrogen, which is deposited on the catalyst, is oxidized and leaves in the form of sulfur oxides ( $\text{SO}_2$  and  $\text{SO}_3$ , hereinafter referred to as "SOx") along with substantial amounts of CO,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

Considerable amount of study and research effort has been directed to reducing oxide of sulfur emissions from various gaseous streams, including those from the stacks of the regenerators of FCC units. However, the results leave much to be desired. Many metallic compounds have been proposed as materials to pick up oxides of sulfur in FCC units (and other desulfurization applications) and a variety of supports, including particles of cracking catalysts and "inerts", have been suggested as carriers for active metallic reactants. Many of the proposed metallic reactants lose effectiveness when subjected to repeated cycling. Thus when Group II metal oxides are impregnated on FCC catalysts or various supports, the activity of the Group II metals is rapidly reduced under the influence of the cyclic conditions. Discrete alumina particles, when combined with silica-containing catalyst particles and subjected to steam at elevated temperatures, e.g., those present in FCC unit regenerators, are of limited effectiveness in reducing SOx emissions. Incorporation of sufficient chromium on an alumina support to improve SOx sorption results in undersirably increased coke and gas production.

Accordingly, an object of the present invention is the provision of an improved composition and process for reducing emissions of sulfur oxides.

An additional object of the present invention  
5 is to provide an improved composition and process for reducing the emissions of sulfur oxides from the regeneration zones of hydrocarbon catalytic cracking units.

Another object of the invention is to provide an improved hydrocarbon conversion catalyst. These  
10 and other objects of the invention will become apparent from the following description and examples.

In one general aspect, the present invention involves a process for combusting solid, sulfur-containing material by contacting the material with gaseous oxygen  
15 in a combustion zone at combustion conditions to produce combustion products including sulfur oxide at least a portion of which is sulfur trioxide. The present improvement comprises carrying out this contacting in the presence of discrete entities containing an effective amount, preferably a  
20 major amount by weight, of at least one metal-containing spinel, preferably alkaline earth metal-containing spinel, to thereby reduce the amount of sulfur oxide (relative to combustion in the essential absence of the discrete entities) emitted from the combustion zone. In another embodiment, the  
25 present improvement comprises carrying out this contacting in the presence of discrete entities containing an effective amount, preferably a major amount by weight, of at least one alkaline earth metal-containing spinel and a minor amount of at least one rare earth metal component associated with the

spinel to thereby reduce the amount of sulfur oxide (relative to combustion in the essential absence of the discrete entities) emitted from the combustion zone.

In accordance with another aspect, the present invention involves a conversion process which is carried out, preferably in the substantial absence of added free hydrogen, in at least one chemical reaction zone in which sulfur-containing hydrocarbon feedstock is contacted with particulate material to form at least one hydrocarbon product and sulfur-containing carbonaceous material deposited on the particulate material and at least one regeneration zone in which at least a portion of the sulfur-containing carbonaceous material deposited on the solid particles is contacted with gaseous oxygen to combust the sulfur-containing carbonaceous material and to produce combustion products including sulfur oxide at least a portion of which is sulfur trioxide.

The present improvement comprises using a particulate material comprising (A) a major amount of solid particles capable of promoting the desired hydrocarbon chemical conversion at hydrocarbon conversion conditions and (B) a minor amount of discrete entities comprising an effective amount, preferably a major amount of weight, i.e., at least about 50% by weight, of at least one metal-containing spinel, preferably alkaline earth metal containing spinel. In the event such discrete entities comprise alkaline earth metal containing spinel, it is more preferred that such discrete entities further comprise

a minor amount of at least one rare earth metal, preferably, cerium, component associated with the spinel. In one preferred embodiment, the discrete entities also include a minor, catalytically effective amount of at least one crystalline aluminosilicate effective to promote hydrocarbon conversion, e.g., cracking at hydrocarbon conversion conditions. The discrete entities are present in an amount sufficient to reduce the amount of sulfur oxides in the regeneration zone effluent when used in a reaction zone-regeneration zone system as described herein.

In one preferred embodiment, the particulate material, more preferably the discrete entities, further comprise a minor amount of at least one additional metal, e.g., a Group VIII platinum group metal, component capable of promoting the oxidation of sulfur dioxide to sulfur trioxide at the conditions in the regeneration zone.

The preferred platinum group metals are palladium and platinum, most preferably platinum.

The preferred relative amounts of the solid particles and discrete entities are about 80 to about 99 parts and 1 to about 20 parts by weight, respectively. This catalyst system is especially effective for the catalytic cracking of a hydrocarbon feedstock to lighter, lower boiling products. The present catalyst system preferably also has improved carbon monoxide oxidation catalytic activity stability.

The improvement of this invention can be used to advantage with the catalyst being disposed in any conventional reactor-regenerator system, in ebullating catalyst bed systems, in systems which involve continuously conveying or circulating catalyst between reaction zone and re-  
5 generation zone and the like. Circulating catalyst systems are preferred. Typical of the circulating catalyst bed systems are the conventional moving bed and fluidized bed reactor-regenerator systems. Both of these circulating  
10 bed systems are conventionally used in hydrocarbon conversion, e.g., hydrocarbon cracking, operations with the fluidized catalyst bed reactor-regenerator systems being preferred.

The catalyst system used in accordance with  
15 certain embodiments of the invention is comprised of a mixture of two types of solid particles.

Although the presently useful solid particles and discrete entities may be used as a physical admixture of separate particles, in one embodiment the discrete  
20 entities are combined as part of the solid particles. That is, the discrete entities, e.g., comprising calcined microspheres containing metal-containing spinel, and preferably, at least one additional metal component, are combined with the solid particles, e.g., during the manufacture of  
25 the solid particles, to form combined particles which function as both the presently useful solid particles and discrete entities is preferably a separate and

distinct phase. One preferred method for providing the combined particles is to calcine the discrete entities prior to incorporating the discrete entities into the combined particles.

5           The form, i.e., particle size, of the present catalyst particles, e.g., both solid particles and discrete entities, as well as the combined particles, is not critical to the present invention and may vary depending, for example, on the type of reaction-regeneration  
10       system employed. Such catalyst particles may be formed into any desired shape such as pills, cakes, extrudates, powders, granules, spheres and the like, using conventional methods. With regard to fluidized catalyst bed systems, it is preferred that the major amount by weight of the present  
15       catalyst particles have a diameter in the range of about 10 microns to about 250 microns, more preferably about 20 microns to about 150 microns.

          The solid particles are capable of promoting the desired hydrocarbon conversion. The solid particles  
20       are further characterized as having a composition (i.e., chemical make-up) which is different from the discrete entities. In one preferred embodiment, the solid particles (or the solid particles portion of the combined particles described above) are substantially free of  
25       metal-containing spinel, e.g., alkaline earth metal-containing spinel.



In one aspect of the present invention, the discrete entities comprise an effective amount of at least one metal-containing spinel, preferably alkaline earth metal-containing spinel, and preferably, a minor, catalytically effective amount of at least one crystalline aluminosilicate capable of promoting hydrocarbon conversion at hydrocarbon conversion conditions. In the event such discrete entities comprise alkaline earth metal-containing spinel, it is more preferred that such discrete entities include a minor amount of at least one rare earth metal component, preferably a cerium component, associated with the spinel. In another aspect of the present invention, the discrete entities, whether present as a separate and distinct particle and/or combined with the solid particles in a single, preferably substantially uniform, mass of combined particles, and/or the solid particles and/or one or more other type of particles (i.e., having compositions different from the present solid particles and discrete entities) further comprise a minor amount of at least one additional metal, e.g., platinum group metal, component capable of promoting the oxidation of sulfur dioxide to the sulfur trioxide at the conditions in the combustion, e.g., catalyst regeneration, zone. For example, an effective amount of at least one sulfur oxide oxidation catalytic component, e.g., metal or compounds of metals selected from Group VI, IIB, IVB, VIA, VIB, VIIA and VIII and mixtures thereof, disposed on a support, e.g., one or more inorganic oxides, may be included with the present solid particles and discrete entities and/or may be included on the solid particles and/or discrete

entities. As noted previously, the sulfur oxide oxidation component may be associated with, e.g., deposited on, the spinel component of the present discrete entities.

The composition of the solid particles useful  
5 in the present invention is not critical, provided  
that such particles are capable of promoting the desired  
hydrocarbon conversion. Particles having widely varying  
compositions are conventionally used as catalyst in  
such hydrocarbon conversion processes, the particular  
10 composition chosen being dependent, for example, on  
the type of hydrocarbon chemical conversion desired.  
Thus, the solid particles suitable for use in the present  
invention include at least one of the natural or synthetic  
materials which are capable of promoting the desired  
15 hydrocarbon chemical conversion. For example, when  
the desired hydrocarbon conversion involves one or  
more of hydrocarbon cracking, disproportionation, isomeri-  
zation, polymerization, alkylation and dealkylation,  
such suitable materials include acid-treated natural  
20 clays such as montmorillonite, kaolin and bentonite  
clays; natural or synthetic amorphous materials, such  
as amorphous silica-alumina, silica-magnesia and silica-  
zirconia composites; crystalline aluminosilicates often  
referred to as zeolites or molecular sieves and the  
25 like. In certain instances, e.g., hydrocarbon cracking  
and disproportionation, the solid particles preferably  
include such crystalline aluminosilicate to increase  
catalytic activity. Methods for preparing such solid  
particles and the combined solid particles-discrete

entities particles are conventional and well known in the art. Certain of these procedures are thoroughly described in U.S. Patents 3,140,253 and RE. 27,639.

Compositions of the solid particles which  
5 are particularly useful in the present invention are those in which the crystalline aluminosilicate is incorporated, in an amount effective to promote the desired hydrocarbon conversion, e.g., a catalytically effective amount, into a porous matrix which comprises, for example,  
10 amorphous material which may or may not be itself capable of promoting such hydrocarbon conversion. Included among such matrix materials are clays and amorphous compositions of silica-alumina, magnesia, zirconia, mixtures of these and the like. The crystalline aluminosilicate  
15 is preferably incorporated into the matrix material in amounts within the range of about 1% to about 75%, more preferably about 2% to about 50%, by weight of the total solid particles. The preparation of crystalline  
20 aluminosilicate-amorphous matrix catalytic materials is described in the above-mentioned patents. Catalytically active crystalline aluminosilicates which are formed during and/or as part of the methods of manufacturing the solid particles, discrete entities and/or combined  
25 particles are within the scope of the present invention.

The solid particles are preferably substantially free of added rare earth metal, e.g., cerium, component disposed on the amorphous matrix material of the catalyst, although such rare earth metal components may be associated with the crystalline aluminosilicate components of the solid particles.

As indicated above, the discrete entities utilized in the present invention comprise an effective amount, preferably a major amount, of at least one metal-containing spinel, preferably alkaline earth metal-containing spinel. In another aspect, the present discrete entities further comprise a minor amount of at least one additional metal, e.g., platinum group metal, component capable of promoting sulfur dioxide oxidation.

The spinel structure is based on a cubic close-packed array of oxide ions. Typically, the crystallographic unit cell of the spinel structure contains 32 oxygen atoms; one-eighth of the tetrahedral holes (of which there are two per anion) are occupied by divalent metal ion, and one-half of the octahedral holes (of which there are two per anion) are occupied by trivalent metal ions.

This typical spinel structure or a modification thereof is adaptable to many other mixed metal oxides of the type  $M^{II}M_2^{III}O_4$  (e.g.,  $FeCr_2O_4$ ,  $BaAl_2O_4$  and  $Co^{II}Co_2^{III}O_4$ ), by some of the type  $M^{IV}M_2^{II}O_4$  (e.g.,  $TiSn_2O_4$ , and  $SnCo_2O_4$ ),

and by some of the type  $M_2^I M^{VI} O_4$  (e.g.,  $Na_2 MoO_4$  and  $Ag_2 MoO_4$ ).

This structure is often symbolized as  $X[Y_2]O_4$ , where square brackets enclose the ions in the octahedral interstices.

An important variant is the inverse spinel structure,

5  $Y[XY]O_4$ , in which half of the Y ions are in tetrahedral interstices and the X ions are in octahedral ones along with the other half of the Y ions. The inverse spinel structure is intended to be included within the scope of the term "metal-containing spinel" as used herein. The  
10 inverse spinel structure occurs often when the X ions have a stronger preference for octahedral coordination than do the Y ions. All  $M^{IV} M_2^{II} O_4$  are inverse, e.g.,  $Sn(SnTi)O_4$ , and many of the  $M^{II} M_2^{III} O_4$  ones are also, e.g.,  $Fe^{III}(Co^{II}Fe^{III})O_4$ ,  $NiAl_2O_4$ ,  $Fe^{III}(Fe^{II}Fe^{III})O_4$  and  $Fe(NiFe)O_4$ . There are also  
15 many compounds with distorted spinel structures in which only a fraction of the X ions are in tetrahedral sites. This occurs when the preference of both X and Y ions for octahedral and tetrahedral sites do not differ markedly.

20 Further details on the spinel structure are described in the following references, which are hereby incorporated herein by reference: "Modern Aspects of Inorganic Chemistry" by H. I. Emeleus and A. G. Sharpe (1973), pp. 57-58 and 512-513; "Structural Inorganic Chemistry", 3rd edition, (1962)  
25 by A. F. Wells, pp. 130, 487-490, 503 and 526; and "Advanced Inorganic Chemistry", 3rd edition, by F. A. Cotton and G. Wilkinson (1972), pp. 54-55.

Metal-containing spinels include the following:

$MnAl_2O_4$ ,  $FeAl_2O_4$ ,  $CoAl_2O_4$ ,  $NiAl_2O_4$ ,  $ZnAl_2O_4$ ,  $MgTiMgO_4$ ,

$\text{FeMgFeO}_4$ ,  $\text{FeTiFeO}_4$ ,  $\text{ZnSnZnO}_4$ ,  $\text{GaMgGaO}_4$ ,  $\text{InMgInO}_4$ ,  $\text{BeLi}_2\text{F}_4$ ,  
 $\text{SLi}_2\text{O}_4$ ,  $\text{MoLi}_2\text{O}_4$ ,  $\text{SnMg}_2\text{O}_4$ ,  $\text{MgAl}_2\text{O}_4$ ,  $\text{CuAl}_2\text{O}_4$ ,  $(\text{LiAl}_5\text{O}_8)$ ,  
 $\text{ZnK}_2(\text{CN})_4$ ,  $\text{CdK}_2(\text{CN})_4$ ,  $\text{HgK}_2(\text{CN})_4$ ,  $\text{ZnTi}_2\text{O}_4$ ,  $\text{FeV}_2\text{O}_4$ ,  $\text{MgCr}_2\text{O}_4$ ,  
 $\text{MnCr}_2\text{O}_4$ ,  $\text{FeCr}_2\text{O}_4$ ,  $\text{CoCr}_2\text{O}_4$ ,  $\text{NiCr}_2\text{O}_4$ ,  $\text{ZnCr}_2\text{O}_4$ ,  $\text{CdCr}_2\text{O}_4$ ,  $\text{MnCr}_2\text{S}_4$ ,  
5  $\text{ZnCr}_2\text{S}_4$ ,  $\text{CdCr}_2\text{S}_4$ ,  $\text{TiMn}_2\text{O}_4$ ,  $\text{MnFe}_2\text{O}_4$ ,  $\text{FeFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$ ,  
 $\text{CuFe}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{CdFe}_2\text{O}_4$ ,  $\text{MgCo}_2\text{O}_4$ ,  $\text{TiCo}_2\text{O}_4$ ,  $\text{CoCo}_2\text{O}_4$ ,  $\text{ZnCo}_2\text{O}_4$ ,  
 $\text{SnCo}_2\text{O}_4$ ,  $\text{CoCo}_2\text{S}_4$ ,  $\text{CuCo}_2\text{S}_4$ ,  $\text{GeNi}_2\text{O}_4$ ,  $\text{NiNi}_2\text{S}_4$ ,  $\text{ZnGa}_2\text{O}_4$ ,  $\text{WAg}_2\text{O}_4$ ,  
and  $\text{ZnSn}_2\text{O}_4$ .

The preferred metal-containing spinels for use  
 10 in the present invention are alkaline earth metal spinels,  
 in particular magnesium aluminate spinel. Lithium containing  
 spinels, which may be produced using conventional techniques  
 are also preferred for use. With regard to magnesium alumi-  
 nate spinel, there often are eight Mg atoms and sixteen Al  
 15 atoms to place in a unit cell ( $8\text{MgAl}_2\text{O}_4$ ). Other alkaline  
 earth metal ions, such as calcium, strontium, barium and mix-  
 tures thereof, may replace all or a part of the magnesium  
 ions. Similarly, other trivalent metal ions, such as iron,  
 chromium, vanadium, manganese, gallium, boron, cobalt and  
 20 mixtures thereof, may replace all or a part of the aluminum  
 ions.

The metal-containing spinels useful in the present  
 invention may be derived from conventional and well known  
 sources. For example, these spinels may be naturally  
 25 occurring or may be synthesized using techniques well known  
 in the art. Thus, a detailed description of such techniques  
 is not included herein. However, a brief description of

the preparation of the most preferred spinel, i.e., magnesium aluminate spinel, is set forth below. Certain of the techniques described, e.g., drying and calcining, have applicability to other metal-containing spinels.

5           The magnesium aluminate spinel suitable for use in the present invention can be prepared, for example, according to the method disclosed in U.S. Patent No. 2,992,191. The spinel can be formed by reacting, in an aqueous medium, a water-soluble magnesium inorganic  
10 salt and a water-soluble aluminum salt in which the aluminum is present in the anion. Suitable salts are exemplified by the strongly acidic magnesium salts such as the chloride, nitrate or sulfate and the water soluble alkali metal aluminates. The magnesium and aluminate  
15 salts are dissolved in an aqueous medium and a spinel precursor is precipitated through neutralization of the aluminate by the acidic magnesium salt. Excesses of acid salt or aluminate are preferably not employed, thus avoiding the precipitation of excess magnesia or alumina.  
20 Preferably, the precipitate is washed free of extraneous ions before being further processed.

The precipitate can be dried and calcined to yield the magnesium aluminate spinel. Drying and calcination may take place simultaneously. However, it is  
25 preferred that the drying take place at a temperature below which water of hydration is removed from the spinel precursor. Thus, this drying may occur at temperatures

below about 500°F., preferably from about 220°F. to about 450°F. Suitable calcination temperatures are exemplified by temperatures ranging from about 800°F. to about 2000°F. or more. Calcination of the spinel precursor may take place in a period of time of at least about one half hour and preferably in a period of time ranging from about 1 hour to about 10 hours.

Another process for producing the presently useful magnesium aluminate spinel is set forth in U.S. Patent 3,791,992. This process includes mixing a solution of a soluble acid salt of divalent magnesium with a solution of an alkali metal aluminate; separating and washing the resulting precipitate; exchanging the washed precipitate with a solution of an ammonium compound to decrease the alkali metal content; followed by washing, drying, forming and calcination steps. The disclosure of U.S. Patent 3,791,992 is hereby incorporated herein by reference. In general, as indicated previously, the metal-containing spinels useful in the present invention may be prepared by methods which are conventional and well known in the art.

The metal spinel-based composition may be formed into particles of any desired shape such as pills, cake, extrudates, powders, granules, spheres, and the like using conventional methods. The size selected for the particles can be dependent upon the intended environment in which the final discrete entities are to be used -- as,



for example, whether in a fixed catalyst bed or circulating catalyst bed reaction system or whether as a separate particle or as part of a mass of combined particles.

Substantially non-interfering proportions of other well known refractory material, e.g., inorganic oxides such as silica, zirconia, thoria and the like may be included in the present discrete entities. Free magnesia and/or alumina (i.e., apart from the alkaline earth metal containing spinel) also may be included in the discrete entities, e.g., using conventional techniques. For example, the discrete entities may include about 0.1% to about 25% by weight of free magnesia (calculated as MgO). By substantially "non-interferring" is meant amounts of other material which do not have a substantial deleterious effect on the present catalyst system or hydrocarbon conversion process. The inclusion of materials such as silica, zirconia, thoria and the like into the present discrete entities may act to improve one or more of the functions of the discrete entities.

The presently useful lithium-containing spinels, e.g., lithium aluminate spinel, preferably are associated with a minor amount of at least one rare earth metal component.

Cerium or other suitable rare earth or rare earth mixture may be associated with the spinel using any suitable technique or combination of techniques; for example, impregnation, coprecipitation, ion-exchange and the like, well known in the art, with impregnation being preferred. Impregnation may be carried out by contacting the spinel with a solution,

preferably aqueous, of rare earth; for example, a solution containing cerium ions (preferably  $\text{Ce}^{+3}$ ,  $\text{Ce}^{+4}$  or mixtures thereof) or a mixture of rare earth cations containing a substantial amount (for example, at least 40%) of cerium ions. Water-soluble sources of rare earth include the nitrate and chloride. Solutions having a concentration of rare earth in the range of 3 to 30% by weight are preferred. Preferably, sufficient rare earth salt is added to incorporate about 0.05 to 25% (weight), more preferably about 0.1 to 15% rare earth, and still more preferably about 1.0 to 15% rare earth, by weight, calculated as elemental metal, on the particles.

It may not be necessary to wash the spinel after certain soluble rare earth salts (such as nitrate or acetate) are added. After impregnation with rare earth salt, the spinel can be dried and calcined to decompose the salt, forming an oxide in the case of nitrate or acetate. Alternatively, the spinel, e.g., in the form of discrete particles, can be charged to a hydrocarbon conversion, e.g., cracking unit, with the rare earth in salt form. In this case a rare earth salt with a thermally decomposable anion can decompose to the oxide in the reactor and be available to associate with  $\text{SO}_x$  in the regenerator.

Especially good results were achieved using spinel containing discrete entities such that the concentration of rare earth metal, e.g., cerium, calculated as the metal, is in the range of about 1 to 25%, more preferably about 2% to about 15%, by weight of the total discrete entities.

The present discrete entities preferably further comprise a minor amount of at least one crystalline aluminosilicate capable of promoting the desired hydrocarbon conversion. Typical aluminosilicates have been described  
5 above. Preferably, such aluminosilicates comprise about 1% to about 30%, more preferably about 1% to about 10%, by weight of the discrete entities. The presence of such aluminosilicates in the present discrete entities acts to increase the overall catalytic activity of the solid  
10 particles-discrete entities mixture for promoting the desired hydrocarbon conversion.

As indicated above, in one preferred embodiment the presently useful particulate material, e.g., the discrete entities utilized in the present invention, also  
15 contain at least one additional metal, e.g., platinum group metal, component. These additional metal components are defined as being capable of promoting the oxidation of sulfur dioxide to sulfur trioxide at combustion conditions, e.g., the conditions present in the catalyst regenerator. Increased  
20 carbon monoxide oxidation may also be obtained by including at least one of the additional metal components. Such metal components are selected from the group consisting of Group IB, IIB, IVB, VIA, VIB, VIIA and VIII of the Periodic Table, the rare earth metals, vanadium, iron, tin and antimony  
25 and mixtures thereof and may be incorporated into the presently useful particulate material, e.g., the discrete entities, in any suitable manner. Many techniques for including the

additional metal in the particulate material are conventional and well known in the art. The additional metal, e.g., platinum group metal, such as platinum, may exist within the particulate material, e.g., discrete entities, at least in part as a compound such as an oxide, sulfide, halide and the like, or in the elemental state. Generally, the amount of the platinum group metal component present in the final discrete entities is small compared to the quantity of the spinel. The platinum group metal component preferably comprises from about 0.05 parts-per-million (ppm) to about 1%, more preferably about 0.05 ppm. to about 1,000 ppm., and still more preferably about 0.5 ppm. to about 500 ppm., by weight of the discrete entities, calculated on an elemental basis. Excellent results are obtained when the discrete entities contain about 50 ppm. to about 200 ppm., and in particular about 50 ppm. to about 90 ppm., by weight of at least one platinum group metal component. The other additional metals may be included in the particulate material in an amount effective to promote the oxidation of at least a portion, preferably a major portion, of the sulfur dioxide present to sulfur trioxide at the conditions of combustion, e.g., conditions present in the catalyst regeneration zone of a hydrocarbon catalytic cracking unit. Preferably, the present discrete entities comprise a minor amount by weight of at least one additional metal component (calculated as elemental metal). Of course the amount of additional metal used will depend, for example, on the

degree of sulfur dioxide oxidation desired and the effectiveness of the additional metal component to promote such oxidation.

Alternately to inclusion in the discrete entities, one or more additional metal components may be present in all or a portion of the above-noted solid particles and/or may be included in a type of particle other than either the present solid particles or discrete entities. For example, separate particles comprising at least one additional metal component and porous inorganic oxide support, e.g., platinum on alumina, may be included along with the solid particle and discrete entities to promote sulfur dioxide oxidation.

The additional metal, e.g., platinum group metal, component may be associated with the spinel based composition in any suitable manner, such as by the impregnation of the spinel at any stage in its preparation and either after or before calcination of the spinel based composition. As indicated previously, various procedures for incorporating the additional metal component or components into the particulate material are conventional and well known in the art. Preferably, the additional metal component is substantially uniformly disposed on the spinel of the present discrete entities. One preferred method for adding the platinum group metal to the spinel involves the utilization of a water soluble compound of the platinum group metal to impregnate the spinel. For example, platinum may be added to the spinel by comingling the spinel with an aqueous

solution of chloroplatinic acid. Other water-soluble compounds of platinum may be employed as impregnation solutions, including, for example, ammonium chloroplatinate and platinum chloride.

Both inorganic and organic compounds of the platinum group metals are useful for incorporating the platinum group metal component into the present discrete entities. Platinum group metal compounds, such as chloroplatinic acid and palladium chloride are preferred.

It may be desirable to be able to separate the discrete entities from the solid particles, for example, when it is desired to use the solid particles alone for hydrocarbon conversion or where it is desired to recover the discrete entities for other uses or for example, for platinum group metal recovery. This can be conveniently accomplished by preparing the second solid particles in a manner such that they have a different size than the first solid particles. The separation of the first and second solid particles can then be easily effected by screening or other means of size segregation.

As noted above, the presently useful solid particles and discrete entities can be employed in a mass of combined particles which function as both the solid particles, e.g., promotes hydrocarbon conversion, and the discrete entities. Such combined particles may be produced in any suitable manner, certain of which methods are conventional and known in the art.

Although this invention is useful in many hydrocarbon chemical conversions, the present

catalyst, i.e., mixture comprising solid particles and discrete entities, and process find particular applicability in systems for the catalytic cracking of hydrocarbons and the regeneration of catalyst so employed. Such

5 catalytic hydrocarbon cracking often involves converting, i.e., cracking, heavier or higher boiling hydrocarbons to gasoline and other lower boiling components, such as hexane, hexene, pentane, pentene, butane, butylene, propane, propylene, ethane, ethylene, methane and mixtures

10 thereof. Often, the substantially hydrocarbon feedstock comprises a gas oil fraction, e.g., derived from petroleum, shale oil, tar sand oil, coal and the like. Such feedstock may comprise a mixture of straight run, e.g., virgin, gas oil. Such gas oil fractions often boil primarily

15 in the range of about 400°F. to about 1000°F. Other substantially hydrocarbon feedstocks, e.g., other high boiling or heavy fractions of petroleum, shale oil, tar sand oil, coal and the like may be cracked using the catalyst and method of the present invention.

20 Such substantially hydrocarbon feedstock often contains minor amounts of contaminants, e.g., sulfur, nitrogen and the like. In one aspect, the present invention involves converting a hydrocarbon feedstock containing sulfur and/or sulfur chemically combined with the molecules

25 of hydrocarbon feedstock. The present invention is particularly useful when the amount of sulfur in such hydrocarbon feedstock is in the range of about 0.01% to about 5%, preferably about 0.1% to about 3%, by weight of the total feedstock.

Hydrocarbon cracking conditions are well known and often include temperatures in the range of about 850°F. to about 1100°F., preferably about 900°F. to about 1050°F. Other reaction conditions usually include pressures of up to about 100 psia.; catalyst to oil ratios of about 1 to 2 to about 25 to 1, preferably about 3 to 1 to about 15 to 1; and weight hourly space velocities (WHSV) of from about 3 to about 60. These hydrocarbon cracking conditions may be varied depending, for example, on the feedstock and solid particles or combined particles being used and the product or products wanted.

In addition, the catalytic hydrocarbon cracking system includes a regeneration zone for restoring the catalytic activity of the solid particles or combined particles of catalyst previously used to promote hydrocarbon cracking. Carbonaceous, in particular sulfur-containing carbonaceous, deposit-containing catalyst particles from the reaction zone are contacted with free oxygen-containing gas in the regeneration zone at conditions to restore or maintain the activity of the catalyst by removing, i.e., combusting, at least a portion of the carbonaceous material from the catalyst particles. When the carbonaceous deposit material contains sulfur, at least one sulfur-containing combustion product is produced in the regeneration zone and may leave the zone with the regenerator flue gas. The conditions at which such free oxygen-containing gas contacting



takes place may vary, for example, over conventional ranges. The temperature in the catalyst regeneration zone of a hydrocarbon cracking system is often in the range of about 900°F. to about 1500°F., preferably about 1100°F. to about 1350°F. and more preferably about 1100°F. to about 1300°F. Other conditions within such regeneration zone may include, for example, pressures up to about 100 psia., average catalyst contact times within the range of about 3 minutes to about 120 minutes, preferably from about 3 minutes to about 75 minutes. Sufficient oxygen is preferably present in the regeneration zone to completely combust the carbon and hydrogen of the carbonaceous deposit material, for example, to carbon dioxide and water. The amount of carbonaceous material deposited on the catalyst in the reaction zone is preferably in the range of about 0.005% to about 15%, more preferably about 0.1% to about 5% by weight of the catalyst. The amount of carbonaceous material deposited on the catalyst in the reaction zone is preferably in the range of about 0.005% to about 15%, more preferably about 0.1% to about 10%, by weight of the catalyst. The amount of sulfur, if any, contained in the carbonaceous deposit material depends, for example, on the amount of sulfur in the hydrocarbon feedstock. This deposit material may contain about 0.01% to about 10% or more by weight of sulfur. At least a portion of the regenerated catalyst is often returned to the hydrocarbon cracking reaction zone.

The solid particles useful in the catalytic hydrocarbon cracking embodiment of the present invention may be any conventional catalyst capable of promoting hydrocarbon cracking at the conditions present in the  
5 reaction zone, i.e., hydrocarbon cracking conditions.

Similarly, the catalytic activity of such solid particles is restored at the conditions present in the regeneration zone. Typical among these conventional catalysts are those which comprise amorphous silica-alumina and at  
10 least one crystalline aluminosilicate having pore diameters of about  $8\text{\AA}$  to about  $15\text{\AA}$  and mixtures thereof. When the solid particles and/or discrete entities to be used in the hydrocarbon cracking embodiment of the present invention contain crystalline aluminosilicate,  
15 the crystalline aluminosilicate may include minor amounts of conventional metal promoters such as the rare earth metals, in particular, cerium.

As indicated previously, one embodiment of the present invention involves contacting solid, sulfur-containing material  
20 in a combustion zone at combustion conditions to produce combustion products including at least one sulfur oxide at least a portion of which is sulfur trioxide. Reduced emissions of sulfur oxide from the combustion zone are achieved by carrying out this contacting in the presence  
25 of discrete entities containing at least one alkaline earth metal spinel and at least one rare earth metal component.

Typical solid material combustion zones include, for example, fluid bed coal burning steam boilers and fluid

sand bed waste combustors. The present discrete entities have sufficient strength to withstand the conditions in such combustion zones. In the coal fired boiler application, the discrete entities are added, either separately or with the sulfur-containing coal, to the combustion zone, e.g., boiler, where combustion takes place and at least some sulfur trioxide is formed. The discrete entities leave the combustion zone with the coal ash and can be separated from the ash, e.g., by screening, density separation, or other well known solids separation techniques. The flue gases leaving the combustion zone have reduced amounts of sulfur oxide, e.g., relative to combustion in the absence of the discrete entities. The discrete entities from the combustion zone can then be subjected to a reducing environment, e.g., contacted with  $H_2$ , at conditions such that at least a portion of the sulfur associated with the discrete entities disassociates with the discrete entities, e.g., in the form of  $H_2S$ , and is removed for further processing, e.g., sulfur recovery. The discrete entities, after sulfur removal may be recycled to the combustion zone, e.g., boiler.

Conditions within the boiler may be those typically used in fluid-bed coal burning boilers. The amount of discrete entities used is sufficient to reduce sulfur oxide emissions in the boiler flue gas, preferably, by at least about 50% and more preferably by at least about 80%. Conditions within the reducing zone are such that at least a portion, preferably at least about 50% and more preferably at least about 80% of the sulfur associated with the discrete entities

is removed. For example, reducing conditions may include temperatures in the range of about 900°F. to about 1800°F.; pressures in the range of about 14 to about 100 psia, and  $H_2$  to associated sulfur mole ratio in the range of about 1 to about 10.

In the fluid sand bed waste combustion application, the fluid sand, e.g., which acts as a heat sink, may be combined with the discrete entities and circulated from the combustion zone to the reduction zone. Reduced emissions of sulfur oxide from the combustion zone are thus achieved.

Conditions in the combustion zone may be as typically employed in fluid sand bed waste combustors. The amount of discrete entities employed is sufficient to reduce sulfur oxide emissions in the combustor flue gases, preferably by at least about 50% and more preferably by at least about 80%. Conditions within the reducing zone are similar to those set forth above for the coal fired boiler application.

The following examples are provided to better illustrate the invention, without limitation, by presenting several specific embodiments of the process of the invention.

#### EXAMPLE I

This example illustrates the production of discrete entities useful in the present invention.

7.05 lb. sodium aluminate (analyzed as 29.8% by weight  $Na_2O$  and 44.85% by weight of  $Al_2O_3$ ) was stirred with one gallon deionized water to bring as much as possible into solution. This was filtered through cloth with a 10" Buchner funnel. The filtered solution was diluted to 8 liters with deionized water.

7.95 lb.  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in one gallon deionized water, and 166 ml. of concentrated  $\text{HNO}_3$  was added. The solution was diluted to 8 liters with deionized water.

5 The two final solutions were run simultaneously from burettes into 32 liters deionized water in a 30 gallon rubber lined drum. The mix was stirred vigorously during the addition. Addition of the  $\text{Mg}(\text{NO}_3)_2$  solution required 36 minutes. 2760 ml. of the sodium aluminate solution was added during this period. The pH was held between 7.0 and 7.5.  
10 After addition of all the magnesium nitrate-containing solution, sodium aluminate solution was added to bring the pH to 8.5. After this, 1080 ml. of sodium aluminate solution remained and was discarded.

The mix was held overnight and then filtered  
15 with a plate-frame press. The cake was washed in the press with 110 gallons deionized water. The cake was reslurried in 10 gallons deionized water. A solution of 26 grams  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 200 ml. deionized water was added to the slurry. The slurry was filtered and washed as before.  
20 After a repeat of the slurry, filter, and wash, the cake was dried at about 250°F. in a forced air drying oven.

The dried product was then hammermilled, first on a 0.050" screen, then the 0-60 mesh portion was hammermilled again, this time on the 0.010" screen. The desirable, fine  
25 material was then screened through a 60 mesh screen. The so-obtained product, magnesium aluminate spinel precursor, was then transferred into a 59 mm diameter quartz tube, where it was calcined, in a fluidized state, for 3 hours

at 900°F. with an air flow rate of about 106 liters per hour to form magnesium aluminate spinel.

The resulting magnesium aluminate spinel particles are screened to produce final particles having diameters less than 100 microns.

#### EXAMPLE II

Example I is repeated except that final magnesium aluminate spinel particles are impregnated, using conventional techniques, with an aqueous solution of chloroplatinic acid. The resulting particles are dried and calcined and contain about 100 ppm. of platinum, by weight of the total platinum-containing particles, calculated as elemental platinum. The platinum is substantially uniformly distributed on the spinel-containing particles.

15

#### EXAMPLE III

Example I was repeated except that the calcined magnesium aluminate spinel was impregnated with cerium.

For cerium impregnation, 0.39 lb. cerium carbonate was slurried in 1820 mls. of water and mixed with 350 mls. of 70% nitric acid slowly to dissolve the carbonate. 3.75 lbs. of the calcined magnesium aluminate spinel was placed in a Pyrex tray and impregnated with the cerium solution with hand mixing using rubber gloves. After the impregnation was complete, the mix was allowed to equilibrate overnight.

The impregnated product was dried under IR lamps and finally in a 260°F. oven overnight. The dried product was calcined in a fluidized state in a 59 mm. diameter quartz reactor, for 3 hours at 900°F. with an air flow rate of about 83 l/hr. The resulting magnesium aluminate

spinel particles were screened to produce final particles having diameters less than 100 microns and these final particles contained 5% by weight of cerium, calculated as elemental cerium.

5

EXAMPLE IV

A quantity of solid particles of a commercially available hydrocarbon cracking catalyst containing about 6% by weight of crystalline aluminosilicate, about 54% by weight amorphous silica-alumina and 40% by weight alpha alumina, and having the same approximate size as the final particles from Example I, is combined with the final particles of Example I so that a mixture of 5 parts by weight of discrete entities and 95 parts by weight of the solid particles results. The catalytic activity of the solid particles is equilibrated by using same (prior to combining with the discrete entities) in commercial fluid bed catalytic cracking service.

10  
15

The mixture of solid particles and final particles is loaded to a conventional fluid bed catalytic cracking unit (FCCU) and used to crack a petroleum derived gas oil fraction, a combined fresh feed and recycle stream. The fresh gas oil fraction boils in the range of about 400°F. to about 1000°F. and is substantially hydrocarbon in nature, containing minor amounts of sulfur and nitrogen as contaminants. Conventional hydrocarbon cracking and catalyst regeneration conditions are employed in the reaction zone and regeneration zone, respectively.

20  
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The weight ratio of catalyst particles to total (fresh plus recycle) hydrocarbon feed entering the reaction zone is about 6 to 1. Other conditions within the reaction zone include:

5	Temperature, °F.	930
	Pressure, psia.	15
	WHSV	15

Such conditions result in about 70% by volume conversion of the gas oil feedstock to products boiling at 400°F. and below.

10 The catalyst particles from the reaction zone include about 0.8% by weight of carbonaceous deposit material which is at least partially combusted in the regeneration zone. This carbonaceous material also includes a minor amount of sulfur which forms SO<sub>2</sub> at the combustion conditions formed in the regeneration zone. Air, in an amount so that amount of oxygen in the regeneration zone is about 1.15 times the amount theoretically required to completely combust this deposit material, is heated to the desired temperature before being admitted to the regeneration zone.

15 Conditions within the regeneration zone include:

	Temperature, °F.	1100
	Pressure, psia.	15
	Average Catalyst	
25	Residence Time, min.	30

After a period of time, the catalyst is shown to remain effective to promote hydrocarbon cracking in the reaction zone, and reduced emissions of sulfur (as sulfur oxides) from the flue gases of the regeneration



zone are obtained (relative to processing in the absence of the final magnesium aluminate spinel-containing particles.)

#### EXAMPLE V

5           Example IV is repeated, except that the platinum-containing particles of Example II are used instead of the magnesium aluminate spinel particles of Example I. After a period of time, the catalyst is shown to remain effective to promote hydrocarbon cracking in the reaction zone and  
10 carbon monoxide and sulfur dioxide oxidation in the regeneration zone. In addition, reduced emissions of sulfur (as sulfur oxides) from the flue gases of the regeneration zone are obtained (relative to processing in the substantial absence of the platinum-containing particles).

15

#### EXAMPLE VI

Example IV is repeated except that the cerium-containing particles of Example III are used in place of the particles of Example I.

After a period of time, the catalyst is shown  
20 to remain effective to promote hydrocarbon cracking in the reaction zone, and reduced emissions of sulfur (as sulfur oxides) from the flue gases of the regeneration zone are obtained (relative to processing in the absence of the final magnesium aluminate spinel-containing particles.)

25

#### EXAMPLE VII

Examples I, II and III are repeated, except that the final magnesium aluminate spinel particles, the platinum-containing particles and the cerium-containing particles, respectively, each include about 7% by weight of a crystal-

line aluminosilicate known to be catalytically active to promote hydrocarbon cracking. The crystalline aluminosilicate is incorporated into the particles using conventional, well known techniques. The platinum, and particularly the cerium, components are included in the particles so that a substantial amount, e.g., greater than about 50%, of the platinum and cerium is associated with the magnesium aluminate spinel of the particles, rather than with the crystalline aluminosilicate. Cerium associated with the crystalline aluminosilicate is substantially less effective, e.g., in reducing SOx emissions, relative to cerium deposited on the magnesium aluminate spinel portion of the particles.

#### EXAMPLE VIII

Example IV is repeated three times except that the magnesium aluminate-containing spinel particles produced in Example VII are used in place of the particles of Example I. After a period of time in hydrocarbon cracking service, these catalyst mixtures are shown to be effective to promote hydrocarbon cracking and reduced sulfur emissions from the regeneration zone are obtained. In particular, it is found that the crystalline aluminosilicate present in the discrete entities improves the hydrocarbon cracking in the reaction zone beyond that occurring in a system with discrete entities containing substantially no zeolitic component.

#### EXAMPLE IX

A mass of combined particles is prepared as follows:

The magnesium aluminate spinel-based discrete entities are prepared by forming an aqueous slurry of magnesium

aluminate spinel precursor (produced as in Example I) so that the spinel concentration, calculated as  $\text{MgAl}_2\text{O}_4$ , is about 9% by weight. Sufficient crystalline aluminosilicate known to be effective to promote hydrocarbon cracking is added to the slurry so that the final magnesium aluminate spinel-based discrete entities contain, on a dry weight basis, about 10% of such crystalline aluminosilicate. This slurry is stirred for about 1 hour to insure uniformity and then spray dried at a temperature less than that required to eliminate a substantial portion of the water of hydration to form discrete entities. These discrete entities are calcined in an electric muffle furnace using a programmed timer to increase the temperature 300°F. per hour to 1050°F. and maintain this temperature for 3 hours. The discrete entities are impregnated with platinum and cerium as in Examples II and III. The final discrete entities contain about 7% by weight of cerium calculated as elemental cerium, and about 100 ppm. by weight of platinum. A major portion of the cerium and platinum is associated with the spinel, rather than the crystalline aluminosilicate.

Essentially all the calcined discrete entities have a maximum dimension of less than about 200 microns. The discrete entities larger than 60 microns are discarded.

The solid particles-binder material is prepared by adding 6000 parts by weight of a solution containing Philadelphia Quartz Company "E" brand sodium silicate solution diluted with an equal weight of water to 3000 parts by weight of dilute (density-1.234)  $\text{H}_2\text{SO}_4$ . After these two solutions are thoroughly mixed, 4000 parts by weight of a solution containing 1200 parts by weight of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  is added. Sufficient crystalline aluminosilicate, known to be effective

to promote hydrocarbon cracking, is added to the mixture so that the final solid particles-binder material contains, on a dry weight basis, about 10% of such crystalline aluminosilicate. The resulting mixture is let stand to gel.

- 5 The resulting hydrogel is cut into about 3/4" cubes and covered with concentrated  $\text{NH}_4\text{OH}$  diluted with an equal volume of water. This material is let stand overnight and has a final pH of 11. The material is then washed by percolation until free of  $\text{Na}^+$  and  $\text{SO}_4^{=}$ ion.

- 10 500 parts (on a dry weight basis) of the washed hydrogel and 80 parts (on a dry weight basis) of the remaining calcined discrete entities and 10,000 parts by weight of water are thoroughly mulled, ground and mixed with agitation. The resulting slurry is dried in a spray drier. This drier
- 15 is equipped with a two-fluid nozzle system which uses air at about 20 psig. to disperse the slurry into the drying chamber. The drying gas, i.e., flue gas from an inline burner, enters the drying chamber at about 750°F. and exits the chamber at a temperature which ranges from about 305°F. to 315°F.
- 20 This drying gas is introduced into the top of the drying chamber while the slurry is dispersed upward from near the bottom of the chamber. In this way, the material to be dried is exposed to both counter-current flow (during ascent from the nozzle system) and co-current flow (during gravity descent)
- 25 relative to the downward drying gas flow. The resulting dried particles are calcined in a manner similar to the calcination of the spinel based discrete entities described above. The

resulting combined particles are screened to provide particles properly sized for use in a fluidized catalytic bed reaction zone-regenerator hydrocarbon cracking system.

EXAMPLE X

5           Example IV is repeated except that the physical mixture of discrete entities and catalyst particles used in Example IV are replaced by the combined particles produced in Example IX. After a period of time, these combined particles are shown to remain effective to promote both hydrocarbon  
10           cracking in the reaction zone and to reduce the amount of sulfur atmospheric emissions in the regeneration zone flue gases.

EXAMPLE XI

15           Example I is repeated except that  $\text{Li}(\text{NO}_3) \cdot 3\text{H}_2\text{O}$  is substituted for the  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The resulting final lithium aluminate spinel particles have diameters less than 100 microns.

EXAMPLE XII

20           The final particles of Example XI are impregnated, using conventional techniques with chloroplatinic acid. The resulting spinel-containing particles are dried and calcined and contain about 100 ppm. of platinum, by weight of the total platinum-containing particles, calculated as elemental  
25           platinum. The platinum is substantially uniformly distributed on the spinel-containing particles.

EXAMPLE XIII

The final particles of Example XI are impregnated, using conventional techniques, with cerium-using as aqueous cerium nitrate solution. The resulting spinel-containing particles are dried and calcined and contain about 10% by weight of cerium, calculated as elemental cerium.

EXAMPLES XIV to XVI

Example IV is repeated three times except that the final particles of Example I are replaced by the resulting spinel-containing particles of Examples XI, XII and XIII, respectively. In each instance, reduced emissions of sulfur (as sulfur oxides) from the flue gases of the regenerator zone is obtained.

EXAMPLES XVII to XXI

Particles having diameters of less than 100 microns of the following spinel materials are prepared using conventional techniques:

<u>Example</u>	<u>Spinel</u>
XVII	$\text{FeAl}_2\text{O}_4$
XVIII	$\text{MnAl}_2\text{O}_4$
XIX	$\text{MgCr}_2\text{O}_4$
XX	$\text{Fe}_2\text{TiO}_4$
XXI	$\text{MgFe}_2\text{O}_4$

EXAMPLES XXII to XXVI

Example IV is repeated five additional times except that the final particles of Example I are replaced by the spinel-containing particles of Examples XVII, XVIII, XIX, XX and XXI, respectively. In each instance, reduced emissions of sulfur (as sulfur oxides) from the flue gases of the re-generator zone is obtained.

EXAMPLES XXVII AND XXVIII

These examples illustrate certain of the surprising benefits of the present invention.

Two blends of particles were prepared for testing. The blends were as follows:

- Blend A - 5% by weight cerium impregnated magnesium aluminate spinel final particles produced as in Example I, plus 95% by weight of a conventional zeolite-containing hydrocarbon cracking catalyst which had been equilibrated in commercial fluid bed catalytic cracking service.
- Blend B - 5% by weight cerium impregnated gamma alumina particles containing 5% by weight of cerium, calculated as elemental cerium, and having a particle size in the range of 25 to 100 microns, plus 95% by weight of the same conventional zeolite-containing catalyst as to prepare blend A. Cerium-alumina particles are known to possess good initial sulfur oxide

removal activity when used in fluid catalytic cracking service.

Both blends were tested to determine their ability to continue to remove sulfur oxides over a period of time.

5 This test procedure was as follows: Step 1 involved an initial determination of the ability of the blend to remove sulfur oxides from regenerator flue gases. Step one was carried out in a fluid bed catalytic cracking pilot plant known to provide results which are correlatable to results obtained  
10 in commercial sized systems. The feedstock and conditions for step 1 were as follows:

- ° Feedstock - mid-continent gas oil containing 2.0% by weight sulfur
- ° Reactor temperature - 930°F.
- 15 ° Regenerator temperature - 1100°F.
- ° Stripper temperature - 930°F.
- ° Pressure - 15 psia.
- ° Approximate catalyst regeneration time - 30 minutes
- ° Approximate stripping time - 10 minutes
- 20 ° Approximate reaction time - 1 minute
- ° Steam as inerts in reactor, 3 mole %.

Step 2 of the test procedure involved continuous and accelerated aging in a fluidized-bed reactor to simulate the type of aging which occurs in commercial fluid-bed  
25 catalytic cracking service. The feedstock and conditions utilized in step 2 were as follows:



- ° Feedstock - Gulf Coast gas oil containing  
2.0% by weight sulfur
  - ° Reactor temperature - 930°F.
  - ° Reactor pressure - 15 psia.
  - 5 ° Reaction residence time - 1 minute
  - ° Reaction catalyst/oil weight ratio - 6
  - ° Stripping temperature - 930°F.
  - ° Regenerator temperature - 1100°F.
  - ° Regenerator pressure - 15 psia.
  - 10 ° Catalyst regenerator residence time - 30
  - ° Regenerator combustion air flow ratio - 20 lbs.air/  
lb.coke
- Step 3 of the test procedure involved periodically

repeating step 1 to determine how much of the blend's  
activity to remove sulfur oxide had been lost during the aging  
15 of step 2.

The amount of sulfur oxides emitted with the flue gases  
from the regeneration using the blend was used as the basis  
for determining the blend's ability (or activity) to remove  
such sulfur oxides.

20 Results of testing Blends A and B following the  
above procedures were as follows:

	Days Aged at Conditions <sup>(1)</sup> of Step 2	% of Initial Activity to Remove Sulfur Oxide Retained	
		<u>Blend A</u>	<u>Blend B</u>
	0	100	100
5	2	93	43
	4	89	18
	6	81	8

(1) One day of aging at the condition of step 2 is more severe than the aging which would occur in commercial FCC service. Therefore, there is no direct one-on-one correlation between aging in these two aging modes.

These results indicate very clearly that the cerium-magnesium aluminate spinel particles of Blend A maintain sulfur oxide removal activity much longer than the cerium-alumina particles of Blend B. Relatively rapid loss of sulfur removal activity has been one of the major problems with prior art attempts, e.g., cerium on alumina particles, to reduce sulfur oxide emissions. Therefore, these results show that the present invention provides substantial and surprising advantages in reducing sulfur oxide emissions from combustion zones, e.g., regeneration zones of fluid bed hydrocarbon catalytic cracking units.

While this invention has been described with respect to various specific examples and embodiments, it is to be understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.

## CLAIMS

1. A composition of matter comprising, in intimate admixture, a major amount of solid particles capable of promoting hydrocarbon conversion at hydrocarbon conditions and a minor amount of discrete entities having a composition different from said solid particles and comprising at least one metal-containing spinel.
2. The composition of claim 1 wherein said hydrocarbon conversion comprises hydrocarbon cracking in the substantial absence of added molecular hydrogen and a major amount, by weight, of said solid particles having diameters in the range of about 10 microns to about 250 microns.
3. The composition of claim 1 or claim 2 wherein said discrete entities contain at least about 70% by weight of said spinel and said spinel has a surface area of about  $25 \text{ m.}^2/\text{gm.}$  to about  $600 \text{ m.}^2/\text{gm.}$
4. The composition of any one of claims 1 to 3 wherein at least one of said solid particles and discrete entities further comprise a minor, catalytically effective amount of at least one additional metal component capable of promoting the conversion of sulfur dioxide to sulfur trioxide.
5. The composition of claim 4 wherein said additional metal component is at least one platinum group metal component.
6. The composition of any one of claims 1 to 5 wherein said spinel comprises alkaline earth metal-containing spinel.
7. The composition of any one of claims 1 to 5 wherein said spinel contains magnesium and aluminum.

8. The composition of any one of claims 1 to 7 wherein said discrete entities comprise at least one alkaline earth metal spinel and at least one rare earth metal component.

9. The composition of claim 8 wherein said spinel contains magnesium and aluminum and said rare earth metal component is a cerium component and is present in an amount in the range of about 1% to about 25% by weight of the total discrete entities.

10. A hydrocarbon conversion process for converting a sulfur-containing hydrocarbon feedstock which comprises (1) contacting said feedstock with solid particles capable of promoting the conversion of said feedstock at hydrocarbon conversion conditions in at least one reaction zone to produce at least one hydrocarbon product and to cause deactivating sulfur-containing carbonaceous material to be formed on said solid particles thereby forming deposit-containing particles; (2) contacting said deposit-containing particles with an oxygen-containing vaporous medium at conditions to combust at least a portion of said carbonaceous deposit material in at least one regeneration zone to thereby regenerate at least a portion of the hydrocarbon conversion catalytic activity of said solid particles and to form a regeneration zone flue gas containing sulfur trioxide; and (3) repeating steps(1) and (2) periodically, characterised in that there is used, in intimate admixture with said solid particles, a minor amount of discrete entities having a composition different from said solid particles and comprising at least one metal-containing spinel, said discrete entities being present in an amount sufficient to reduce the amount of sulfur oxides in said flue gas.

11. The process of claim 10 wherein said discrete entities comprise at least one alkaline earth metal-containing spinel and at least one rare earth metal component associated with said spinel.
12. The process of claim 11 wherein said rare earth metal component comprises cerium.
13. The process of claim 12 wherein said rare earth metal component is cerium component and is present in an amount of about 1% to about 25% by weight of said discrete entities.
14. The process of any one of claims 10 to 13 wherein said conversion comprises hydrocarbon cracking in the substantial absence of added molecular hydrogen, said solid particles and discrete entities being fluidizable and circulating between said reaction zone and said regeneration zone.
15. The process of any one of claims 10 to 14 wherein said discrete entities contain at least about 70% by weight of said spinel and said spinel has a surface area of about  $25 \text{ m.}^2/\text{gm.}$  to about  $600 \text{ m.}^2/\text{gm.}$
16. The process of any one of claims 10 to 15 wherein at least one of said solid particles and discrete entities further comprises a minor, catalytically effective amount of at least one additional metal component capable of promoting the conversion of sulfur dioxide to sulfur trioxide at the conditions of step (2).
17. The process of claim 16 wherein said additional metal component is at least one platinum group metal component.
18. The process of any one of claims 10 to 17 wherein said spinel comprises alkaline earth metal-containing spinel.

19. The process of claim 18 wherein said spinel contains magnesium and aluminum.

20. The process of any one of claims 10 to 19 wherein said discrete entities contain at least about 90% by weight of said spinel.

21. A process as claimed in claim 10 in which said feedstock is contacted in step (1) with a composition as claimed in any one of claims 1 to 9.

22. A process for combusting solid, sulfur-containing material by contacting said material with gaseous oxygen in a combustion zone at combustion conditions to produce combustion products including at least one sulfur oxide, characterised in that said contacting is carried out in the presence of discrete particles containing a major amount of metal-containing spinel, thereby reducing the amount of sulfur oxide emitted from said combustion zone.

23. A process for combusting solid, sulfur-containing material by contacting said material with gaseous oxygen in a combustion zone at combustion conditions to produce combustion products including at least one sulfur oxide, characterised in that said contacting is carried out in the presence of discrete particles containing a major amount of alkaline earth metal-containing spinel and a minor amount of at least one rare earth metal component, thereby reducing the amount of sulfur oxide emitted from said combustion zone.

0045170



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application number

EP 81 30 3336

DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages		TECHNICAL FIELDS SEARCHED (Int. Cl.)
	<p><u>US - A - 4 055 513</u> (KENNETH W. WHEELLOCK)</p> <p>* column 2, line 1 - column 3, line 60; claims 1,8,9,10 *</p> <p>--</p> <p><u>GB - A - 2 023 639</u> (ATLANTIC RICH-FIELD COMP.)</p> <p>* page 4, line 127 - page 5, line 36; claims 19,20,28-30, 35, 42-44 *</p> <p>--</p> <p><u>DE - A - 1 952 232</u> (BORIS P. KOMILOV)</p> <p>* page 1, lines 1-11; claims 1,2 *</p> <p>--</p> <p><u>GB - A - 1 561 629</u> (IMPERIAL CHEMICAL IND.)</p> <p>* page 4, lines 1-48; claims 1-3,23 *</p> <p>--</p> <p><u>EP - A - 0 010 362</u> (MOBIL OIL CORP)</p> <p>* page 1, line 1 - page 2, line 10; page 5, lines 11-20; claims 1,2,8 *</p> <p>--</p> <p><u>US - A - 4 191 115</u> (RALPH, T. YANG et al.)</p> <p>* examples I, IV; claims 1,13,16, 22,33-35 *---</p>	<p>1,6,7,8</p> <p>1,4,5,10,14,16,17</p> <p>1,6,7</p> <p>1</p> <p>1,8,9,10-12,14</p> <p>22</p>	<p>B 01 J 21/00 C 10 G 11/04 C 10 L 10/00</p> <p>B 01 J 21/00 23/00 37/04 C 10 G 11/04 11/05 C 10 L 9/10 10/00</p> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons</p> <p>&amp;: member of the same patent family, corresponding document</p>
<p><input checked="" type="checkbox"/> The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
The Hague	11-11-1981	HÖFER	